

VENUS ATMOSPHERE BUILD-UP AND EVOLUTION : WHERE DID THE OXYGEN GO? MAY ABIOTIC OXYGEN-RICH ATMOSPHERES EXIST ON EXTRASOLAR PLANETS? RATIONALE FOR A VENUS ENTRY PROBE

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ABSTRACT

The build-up of the massive atmosphere of Venus is still poorly understood. The evaporation of a primitive ocean may have resulted in a strong water vapor greenhouse effect, followed by hydrodynamic escape of hydrogen. The fate of the large amounts of oxygen left behind is still unknown. The absence of O₂ in the present Venus atmosphere shows that all the primitive oxygen has been removed. Has it been added to the crust through oxidation, or was early hydrodynamic escape strong enough to drag off oxygen along with hydrogen? If oxygen would not have been lost, Venus atmosphere would be rich in abiotic oxygen. Understanding what was the fate of Venus oxygen is therefore crucial for interpreting possible future observations by DARWIN of oxygen-rich extrasolar atmospheres. A mission to Venus consisting of a descent probe, equipped with noble gas and chemical sensors, and IR spectro-imagers, would greatly help in answering the questions : How much water was Venus endowed with, and where did the oxygen go? May abiotic oxygen-rich atmospheres exist on extrasolar planets?

Keywords : Venus, runaway greenhouse, water, abiotic oxygen, extrasolar planets.

1. INTRODUCTION

It is thought that the massive greenhouse effect observed today in Venus atmosphere was initiated by the evaporation of an ocean of water at early times ([1], [2]) that is a few millions to ten millions years after (and/or during) the formation of the planet. Because water could not condense at temperatures prevailing in the inner solar nebula, planets have been supplied with water by impacting meteorites and/or comets during an extended period after the main accretion period. The primary source of water was located in the outer solar system, beyond Jupiter's orbit, and the three terrestrial

planets should have been endowed with similar quantities of water. Nevertheless, because the impact of a large body results in the release to space of substantial amounts of atmosphere, the net budget of accreted water cannot be calculated in a simple way. From [3] it comes that the incoming water flux on Venus and Earth was in excess of the outgoing one. On the base of existing models, this excess is expected to be larger for Venus and the favored scenario is therefore that Venus accreted at least as much water as Earth.

It has been shown by [4] that, due to the large amounts of water vapor expected to be present in the early Venus atmosphere, photolysis of water molecules followed by hydrodynamic escape of hydrogen is able to remove the total hydrogen content of the ocean in less than 2 Gyr. What was the fate of the oxygen atoms produced by photolysis of water molecules? In the case of a large hydrogen escape flux, heavier species like oxygen can be dragged off along with hydrogen, according to the theory developed by [5]. Nevertheless, even by taking into account the higher values of the solar EUV flux at early epochs ([6]), the amount of oxygen lost is not expected to exceed ≈25% of the total ocean content ([7]). By assuming a relatively moderate value of the hydrogen density at the base of the expansion (according to [4]), only photons at wavelengths longer than ≈50 nm play a significant role in powering escape, which therefore works a factor of 3-4 below the EUV energy limited rate. By considering the solar EUV flux as the only source of escape energy, the amount of oxygen left behind escaping hydrogen would not exceed in this case a few percents.

There are two ways to explain the lack of oxygen in the present Venus atmosphere: (1) Venus was initially endowed with less water than Earth, which seems unlikely; (2) Venus was supplied with as much water as Earth (or more), in agreement with

our general understanding of solar system formation, and oxygen was lost, either by oxidation of the crust, or by escape to space. Oxidation of FeO, and possibly metallic iron, contained in surface basalts could have been able to remove oxygen over geological times provided resurfacing processes were as much efficient as on Earth (see Section 3), which seems unlikely. Massive escape to space is also possible, but it requires an extra source of energy, in addition to EUV solar radiation. This source could be the solar wind, according to a process involving charge exchange between escaping neutral atoms and solar wind protons ([8]), possibly helped by intense sputtering. A strong primitive solar wind, with an enhancement factor up to 4 orders of magnitude with respect to the present one (see e.g. [9]), is potentially able to stimulate a flux high enough for oxygen atoms to be massively dragged off along with hydrogen atoms ([10]).

2. LOSS OF OXYGEN BY HYDRODYNAMIC ESCAPE

In order to correctly assess the assumption that oxygen was lost to space by hydrodynamic escape, it is necessary to better constrain primitive hydrodynamic escape on Venus through noble gas elemental and isotopic measurements.

2.1. Clues to an early hydrodynamic escape on terrestrial planets

The theory of the hydrodynamic escape has been developed by [5] and applied to mass fractionation of planetary atmospheres by [11] and [12]. Hydrodynamic escape consists of a global, cometary-like, expansion of the atmosphere. It happens when a large amount of energy (solar EUV and/or solar wind) is deposited at the top of the atmosphere, allowing heated atoms to overcome the gravity field of the planet and to expand into the interplanetary space. An heavy constituent “2”, of mass m_2 and mixing ratio X_2 , is dragged off along with a light escaping constituent “1” (H or H₂), of mass m_1 and mixing ratio X_1 , according to the following law ([12]): $F_2 = X_2/X_1 F_1 (m_c - m_2)/(m_c - m_1)$, where F_i are the fluxes (and: $m_c = m_1 + (kTF_1/bgX_1)$) is the “crossover mass” (b is the product of the density by the diffusion coefficient of “2” in “1”). If $m_2 < m_c$, “2” can escape with “1” (the flux F_2 is proportional to the difference $m_c - m_2$). Assuming that all the EUV flux is consumed in escape (energy-limited rate), it is possible to calculate the crossover mass for present solar EUV conditions: 1.5 amu (amu: atomic mass unit) for Earth, 5 amu for Mars.

There are only a few clues to the effective occurrence of hydrodynamic escape on planets at the beginning of their life.

Isotopic fractionation of xenon in Earth and Mars atmospheres

It is generally accepted, although not proved, that hydrodynamic escape could be responsible for the enrichment of heavy xenon isotopes in Earth and Mars atmospheres (as measured in SNC gas inclusions for Mars), as shown in Figure 1. Hydrodynamic escape occurs when the EUV solar flux is very large. In this case, the energetic balance equation of the high atmosphere has no static solution (unlike the classical case of Jeans escape), which could happen at the beginning of solar system history ([6]). In this case, escape must be treated like a hydrodynamic process involving the atmosphere as a whole ([17]). EUV-powered escape is expected to have been able to deplete and isotopically fractionate Ne (on Earth), and possibly also Ar on Venus, over long periods of time (≈ 100 Myr). On Earth, the giant impact at the origin of Moon’s formation may have resulted in a strong and short period of intense (GI-driven) hydrodynamic escape ([13]), with depletion and fractionation of heavy elements (Kr, Xe). Finally, in the case of a non-magnetized or weakly magnetized plane Solar-Wind-driven hydrodynamic escape may occur through sputtering of the high atmosphere, either by solar ions ([8]), or by planetary pick-up ions, and result in escape of oxygen and other light species.

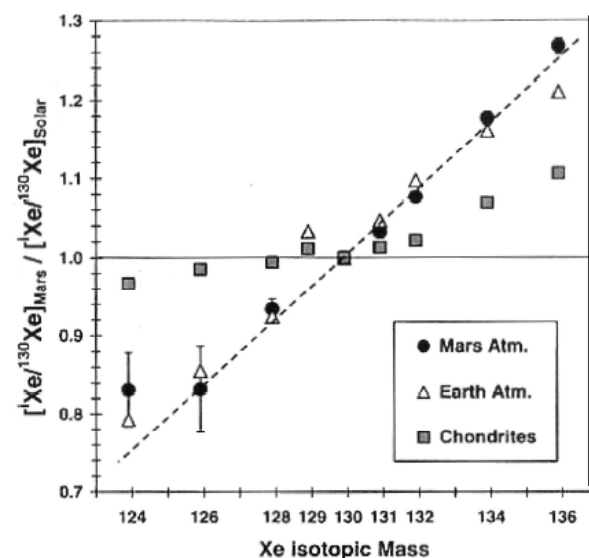


Figure 1 : Mass isotopic fractionation patterns of xenon in Earth atmosphere, Mars atmosphere and chondrites. Mars values are obtained from SNC meteorites (from [14]).

The paradox of lacking oxygen in Venus atmosphere

The absence of molecular oxygen at substantial level in the atmosphere of Venus is still poorly understood. It is thought that very high temperature and pressure at the surface of Venus have been initiated by the evaporation of an ocean of water at early times ([2]). Such a process would have resulted in a dense steam atmosphere (a few hundred bars) generating a strong greenhouse effect preventing carbon dioxide from forming carbonates (unlike Earth: the equivalent of a few tens bars of CO₂ are estimated to be trapped in sedimentary rocks of oceanic floors). During an episode of primitive greenhouse, photodissociation of water molecules followed by escape of hydrogen is in principle able to remove the total hydrogen content of the ocean ([15], [16]). [4], following [17], shown that it may occur over one or two billion years through hydrodynamic escape. But what was the fate of the oxygen atoms contained in water molecules? In the case of an intense hydrogen escape flux, heavier species like oxygen can be dragged off along with hydrogen, according to the theory developed by [5].

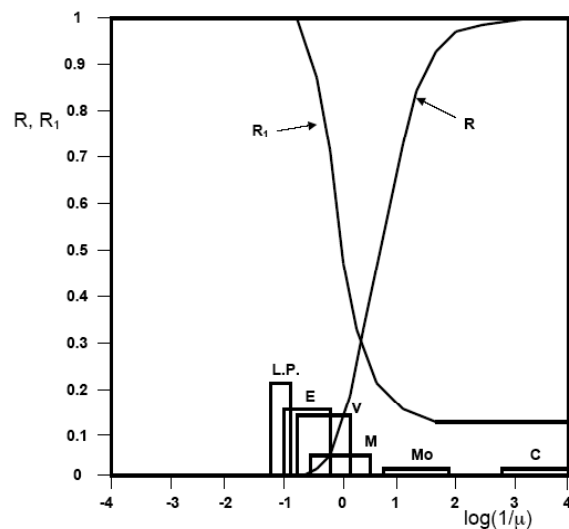


Figure 2 : Ratio R of O lost amount to twice H lost amount as a function of a crossover mass-related parameter : $\log(1/\mu)$ (from [7]).

[7] assumed a period of hydrodynamic escape extending over the first billion years. The EUV flux is supposed to vary with time t as $(t_0/t)^{5/6}$, where t_0 is the present time (4.6 Gyr). The crossover mass m_c is assumed to vary with time due to the decrease of solar EUV flux according to the energy-limited approach. Denoting by μ the parameter $m_2/m_c = 16/m_c$ (species “2” is atomic oxygen in this case) at the end of hydrodynamic escape phase (assumed to be $t = 1$ Gyr in this calculation), and R the ratio of O lost amount to 2 times H lost amount (cumulated over the first billion years), the relationship between

R and $\log(1/\mu)$ is shown in Figure 2 for different bodies: Ceres-type asteroid, Moon, Mars, Venus, Earth, and a large Earth-like exoplanet (twice Earth radius). The ratio R_1 between the H amount lost assuming O is dragged-off together (which requires 9 times more energy than if H alone is lost) and the H amount lost with no simultaneous O escape is also plotted. Plausible $\log(1/\mu)$ -ranges are shown for the different considered bodies at $t=1$ Gyr. They take into account the planet-Sun distance (controlling the amount of EUV flux received by unit surface) and the size of the planet (determining its gravitational field), and include uncertainties of different natures (the widths of the boxes are representative of the uncertainties). This figure shows that small bodies, including Mars, may lose much of their oxygen through a runaway greenhouse-type primitive episode, but that the loss is only partial for Venus and Earth, and not effective for a large terrestrial-type exoplanet. A consequence of this calculation is that a primitive runaway greenhouse may theoretically generate a massive abiotic oxygen atmosphere, provided the planet is large enough (radius > 1.5 Earth radius) for its gravitational field to prevent hydrodynamic oxygen escape.

2.2. Noble gases as tracers of the formation and evolution of planetary atmospheres

The primary atmospheres of the terrestrial planets may be, either derived by outgassing from the solid interior, or accreted from the outside (e.g. addition of cometary material). Secondary processes such as escape, outgassing from the solid planet, radiogenic contribution, solar wind addition, sputtering, chemical conversion (carbonate precipitation, photosynthesis, water decomposition etc...) may have significantly altered their primary composition. Noble gases are ideal tracers to understand the formation and evolution of the atmospheres of terrestrial planets. Their chemical inertness and the presence of numerous isotopes among which radiogenic ones (e.g. ⁴He, ⁴⁰Ar), nucleogenic ones (e.g. ²¹Ne) and fissiogenic ones (¹³⁴⁻¹³⁶Xe) permit to identify a number of possible sources to planetary atmospheres as well as the fingerprint of physical processes previously mentioned. Unlike chemical compounds, they can be found in the atmospheres of the terrestrial planets, in meteorites of various types and in the solar wind. Attempts at modelling the terrestrial atmospheric evolution have confirmed the high potentiality of these elements.

The composition of Venus atmosphere according to the previous measurements by Pioneer and Venera missions is : CO₂ (96.5 %), N₂ (3.5%), ⁴⁰Ar (31 ppm), He (12 ppm), Ne (7 ppm), ³⁶Ar (30 ppm), Kr (25 ppb), Xe (<10 ppb). Uncertainties on noble gas

abundances are large (factor 2 to 10, see Wieler, 2002). The isotopic ratios of Ne and Ar are known with some uncertainties, suggesting an enrichment of ^{22}Ne with respect to ^{20}Ne relative to Earth ($\approx 20\%$), and a similar $^{36}\text{Ar}/^{38}\text{Ar}$. But it is worth considering a confirmation because of possible interferences (e.g. with HCl). Therefore estimates of He, Ne, Kr and Xe isotopes would provide invaluable information necessary for comparative planetology and to constrain models of atmospheric formation and evolution (for both Venus and Earth).

- Helium: the abundance and isotopic composition of helium results from the competition between : (i) outgassing from the solid interior ; (ii) escape from the atmosphere ; (iii) input from solar wind. On Earth, outgassing from the solid interior consists of two well identified fluxes: one rich in ^3He (primordial) from the mantle and a purely radiogenic one in relation with crustal outgassing. The same components will have to be considered on Venus but with a completely different relative importance: volcanism on Earth in relation with plate tectonics is a major phenomenon. Release from the crust is a rapid process because of erosion. On Venus the much higher temperature should promote escape from deeper crustal layers but how does erosion play a role? Input from the solar wind is limited on Earth because of the magnetic field. The absence of a significant field on Venus will have an influence on the abundance and isotopic composition of He in Venus atmosphere.

- Neon: in the terrestrial atmosphere, Ne isotopes are intermediate between a planetary component (chondritic) and a solar component. The question is whether this results from mixing of these two components (mantle Ne is solar) or more simply, from mass fractionation as a result of massive escape from the atmosphere in its early stages. Measuring Ne isotopes in the atmosphere of Venus will greatly help constraining such problems.

- Argon: ^{40}Ar is the radiogenic product of ^{40}K . On Earth, it is a major component of the atmosphere (1%), testifying of the importance of outgassing. On Venus, ^{40}Ar is less abundant than on Earth while ^{36}Ar is far more abundant, illustrating a drastic difference between the two planets. Where does ^{36}Ar come from? Its ratio to Ne precludes a significant solar contribution. Its total abundance corresponds to what is recorded in the most gas rich chondrites, a very surprising result.

- Krypton and Xenon: Krypton isotopes may provide some information on the escape processes because of the possibly mass fractionated pattern easy to interpret in the absence of radiogenic/ nucleogenic contributions. Its ratio to Ar and Xe would permit to characterize its source in Venus atmosphere. Xenon carries more information than anyone of the other noble gases because of its numerous isotopes including radiogenic/ fissiogenic isotopes from short

and long lived parents. Is the terrestrial missing xenon a unique signature of our planet? Does Venus exhibit isotopic anomalies in ^{129}Xe , $^{134-136}\text{Xe}$? Are Venus atmospheric Xe isotopes mass fractionated relative to the Earth/Solar references?

2.3. Inferences from Martian noble gases measurements

The abundances of noble gases measured in Mars atmosphere are displayed in table 1. All of them but He have been measured by mass spectrometry on Viking landers ([18]). Because of its permanent escape, He cannot be used as a tracer of Mars past evolution. On the opposite, neon, argon, krypton and xenon are reliable tracers. A noticeable deficiency of Mars relative to the Earth is clearly revealed in Figure 3. The observed combination suggests a fractionating depletion by escape, which can be more effective on Mars because of the weaker gravity field. This conclusion is consistent with the results obtained for major components.

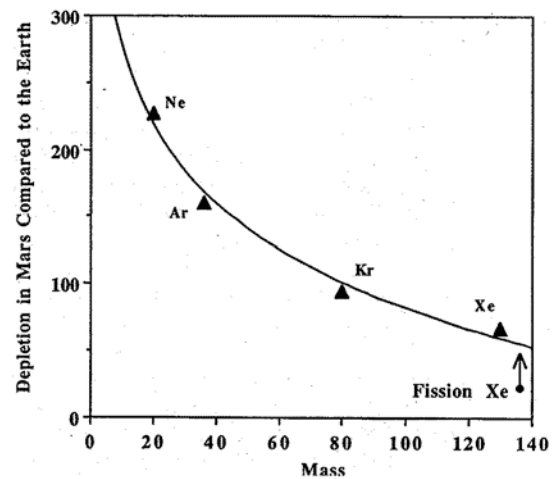


Figure 3 : Depletion of noble gases in the Martian atmosphere compared to Earth (from [19]).

Noble gas isotopic spectra bring additional information, allowing to get rid of possible compositional differences at the beginning. [20] suggest that noble gas abundance in carbonaceous chondrites was initially similar to that of enstatite chondrites (such as S. Oman), which in turn resembles that of Earth and Mars atmospheres (relative deficiency in xenon). Chondrites or their parent bodies would have subsequently lost some of their noble gases by diffusion, a process favoring the loss of light gases (Ne and Ar) relative to heavy ones (Kr and Xe). Comparing the isotopes of one gas permits to minimize initial differences in planetesimals.

Concerning Mars, there is one single measurement of a ratio between non-radiogenic isotopes, i.e.

$^{36}\text{Ar}/^{38}\text{Ar}$ (see table 1). The Viking value is identical (within the error bars) to the terrestrial and chondritic values, unlike the atypical value given by SNC. The relative enrichment of ^{38}Ar in SNC has been considered as an evidence of atmospheric escape (mainly sputtering, still active at present time). Detailed studies on noble gas isotopes (especially Kr and Xe) rely on the analyses of trapped gas in SNC meteorites because of the lack of in-situ measurements. These studies reveal the great complexity of isotope fractionation (Pepin and Carr, 1992). For instance, isotopic fractionation for one species are generally not consistent with elemental fractionation between different species. The major question to be solved is whether compositional differences, both elementary and isotopic, between the Earth, Mars and Venus reflect differences already present in their planetesimal parents or whether fractionation processes related to outgassing, atmospheric escape during accretion or later may have modified the pre-planetary composition. This question raised by [21] is far from being solved. The compositional differences between the three planets might result from initial variability among planetesimals. If so, the contrasting abundances could be explained by escape, under its different forms (hydrodynamic, non-thermal), occurring after outgassing, without fractionation (or with only small fractionation).

Table 1 : Noble gas isotopic compositions*

Ratio	Viking	SNC	Earth
$^{20}\text{Ne}/^{22}\text{Ne}$		7 - 11	9.8
$^{21}\text{Ne}/^{22}\text{Ne}$		< 0.15	0.029
$^{36}\text{Ar}/^{38}\text{Ar}$	5,5±1,5	3.4 - 4.0	5,32
$^{40}\text{Ar}/^{36}\text{Ar}$	3000±500	1900±100	295.5
$^{82}\text{Kr}/^{84}\text{Kr}$		~0.210	0.20217
$^{83}\text{Kr}/^{84}\text{Kr}$		~0.205	0.20136
$^{86}\text{Kr}/^{84}\text{Kr}$		~0.296	0.30524
$^{129}\text{Xe}/^{132}\text{Xe}$	2,5 (+2, -1)	2,60±0,05	0,983
$^{131}\text{Xe}/^{132}\text{Xe}$		~0.8	0,789
$^{134}\text{Xe}/^{132}\text{Xe}$		~0,4	0,389
$^{136}\text{Xe}/^{132}\text{Xe}$		~0,4	0,329

*Sources: [22], [23], [24].

A different and complementary approach consists of assuming that the noble gas composition of planetesimals, parent to planetary bodies, is the same for the various planets (e.g. that of carbonaceous chondrites) and that present day Mars atmosphere results from successive fractionation steps from the post accretion period to the present time. It is generally accepted that EUV-driven (and possibly SW-driven) hydrodynamic escape could be responsible for xenon heavy isotope enrichment on both Earth and Mars. As shown by [12], it is possible, from theoretical models, to obtain a fractionation pattern of xenon matching the observed

one. Assuming that the EUV flux evolved with time like $(t_0/t)^{5/6}$ ([6]), it can be calculated that the crossover mass m_c is larger than Xe mass at very early ages (the few first Myr), which potentially allows substantial hydrodynamic escape of xenon during the first ten millions years of Earth life (it is similarly true for Mars). But it requires a tremendous quantity of hydrogen (the equivalent of a 30 km deep ocean) to have been removed by carrying with it, almost completely, other components like Kr, Ar and Ne. In the model of [12], argon and neon are depleted by factors of 30 and 50 respectively relative to krypton, which is inconsistent with observations. In addition, Kr in SNCs is isotopically lighter than terrestrial or chondritic Kr, the opposite of what is observed for xenon.

In order to clear up the above inconsistencies, it seems necessary to introduce several phases of hydrodynamic escape, like proposed by [25], following the paper by [26]. These authors shown that, by mixing a fractionated Xe component of the residual primordial atmosphere and an unfractionated Xe component contained originally inside the Earth, it is possible to mimic Earth Xe fractionation pattern. In the extensive model proposed by [27], xenon is similarly the residue of an hydrogen rich primary atmosphere bound by gravitational forces to the solid planet in its accretion stage, whereas lighter gases result from outgassing at a later stage. Two stages of hydrodynamic escape are required to fractionate xenon (primordial), then the lighter noble gases like Kr and Ar outgassed after the first stage of escape (secondary). The first stage may result from the Moon-forming giant impact. The second stage of (EUV-powered) hydrodynamic escape should however be of moderate magnitude to avoid the fractionation of Kr, whose pattern is nearly solar-like. Finally, non-thermal escape takes over during a later stage, leading to the presently observed pattern for major gases ([28]; see also [19]).

Because most of the noble gas isotopic ratios are derived from SNC measurements, and due to the fact that the Martian origin of SNCs is not proved, and that even if SNCs are from Martian origin some fractionation could occur with respect to the free atmosphere, in-situ measurements of noble gases on Mars are strongly required to investigate further the history of Martian atmosphere.

2.4. Venus noble gases : a key measurement for understanding the history of terrestrial atmospheres

Noble gases in the Venusian atmosphere have been analyzed by mass spectrometry and gas

chromatography on board Pioneer Venus and several Venera probes. The data are displayed in Table 2.

The relative elemental abundances of the four heavier noble gases for the three terrestrial planets and CI chondrites are displayed in Fig. 4. Although a similar pattern is observed for the three planets, there are several significant differences. Ne and Ar are significantly more abundant than in Earth atmosphere, by at least factors 10 and 50, respectively. The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio is depleted by a factor of ≈ 3 in Venus atmosphere relative to Earth. The Venus noble gas elemental spectrum is much more solar-like than those of Earth and Mars, Ar being slightly (factor 10) depleted with respect to the Sun, whereas Ne is strongly depleted (factor 1000).

Table 2 : Noble gases in the atmosphere of Venus (from [29])

Element	Venus value	Earth value
Radiogenic isotopes (mixing ratios)		
^4He (ppm)	0.6-12	
^{40}Ar (ppm)	21-51	
^{129}Xe (ppb)	<9.5	
Venus/Earth (abundance ratio)		
^4He	175-3700	
^{40}Ar	0.25	
Non-radiogenic isotopes (mixing ratios)		
^{20}Ne (ppm)	4-13	
^{36}Ar (ppm)	21-48	
^{84}Xe (ppb)	7-38	
^{132}Xe (ppb)	<10	
Venus/Earth (abundance ratio)		
^{20}Ne	21 [10-40]	
^{36}Ar	70 [50-110]	
^{84}Kr	3 [1-5]	
^{132}Xe	<35	
Isotopic ratios		
$^3\text{He}/^4\text{He}$	$<3 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
$^{20}\text{Ne}/^{22}\text{Ne}$	11.2-12.6	9.8
$^{21}\text{Ne}/^{22}\text{Ne}$	<0.067	0.029
$^{36}\text{Ar}/^{38}\text{Ar}$	5.45 ± 0.1	5.32
$^{40}\text{Ar}/^{36}\text{Ar}$	1.11 ± 0.02	295.5

The Venus pattern is quite different of the chondritic one, which resembles Earth and Mars patterns. It may be seen that the amount of carbon (in CO_2) and nitrogen (in N_2) are similar on Earth and Venus (when terrestrial carbonates are taken into account), but that they are depleted by two orders of magnitude on Mars. The relative similarities of CO_2 , N_2 , Kr and Xe on Venus and Earth, compared to Mars (depleted by a factor ≈ 100) suggest that Mars experienced a much stronger atmospheric escape (probably due to its smaller size). The enhancement of Venus atmosphere in Ne and Ar (by a factor of ≈ 100) with respect to Earth, which may be interpreted as a more solar-like composition, and the fact that Venus is different of the two other planets and chondrites, suggests a direct supply by solar wind. The solar wind component could be mixed

with a chondritic component but, due to the large uncertainties on Kr and Xe elemental abundances in Venus atmosphere, any quantitative estimate of the relative contributions of the solar and chondritic components is difficult. A more precise measurement of elemental abundances is required for Kr and Xe.

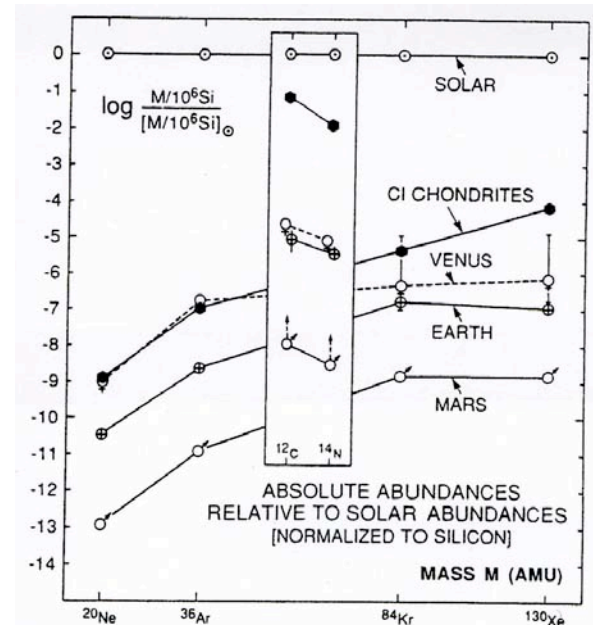


Figure 4 : relative elemental abundances of the four heavier noble gases in the Martian atmosphere, compared with terrestrial atmosphere and meteorites, all plotted relative to solar abundances (from [13]).

Interestingly, Ne is by far the most depleted noble gas in Venus atmosphere, and is also depleted by a factor of 3 with respect to Earth, Mars and chondrites, despite the large error bar. Such a depletion, in both absolute and relative ways, might be associated to a phase of EUV-driven (and possibly SW-driven) hydrodynamic escape of only Ne, which could have extended over several hundred million years. Because Ne ($m=20$) is slightly heavier than O ($m=16$), hydrodynamic escape of Ne, if it occurs ($m_c > 20$), implies hydrodynamic escape of oxygen, and Ne might be used as a tracer of oxygen escape at primitive stages. The fact that Ne is isotopically heavier on Venus than on Earth (whereas Ar is not) is consistent with a period of hydrodynamic escape of Ne only, but more precise modeling would have to be done to explore the impact of a phase of hydrodynamic escape of H (and O) on the Ne elemental and isotopic abundances.

It is therefore of paramount importance to accurately measure :

- the elemental abundances of noble gases on Venus, in order to get a reliable comparison with other terrestrial planets and meteorites,
- the isotopic spectra of Xe and Kr, in order to check the assumption of a dominant solar origin for Venus noble gases, and to compare with Earth and Mars case,
- the isotopic composition of Ar and Ne for constraining models of moderate hydrodynamic escape removing hydrogen, and possibly oxygen, from the young Venus atmosphere, following a “runaway” or “moist” greenhouse period.

More generally, such a measurement would allow to discriminate between pre-planetary (within planetesimals) and post-accretional (in planetary atmospheres) fractionation scenarios, and to reconstruct in a reliable way the history of volatiles on the three planets.

Concerning isotopes of light elements : H, C, N and O, they exhibit highly variable isotopic compositions depending on the diverse chondrite classes and planetary objects. They result from: (i) nucleosynthetic processes ; (ii) heterogeneity in the Solar nebula ; (iii) fractionation processes upon accretion ; (iv) differentiation and evolution of planetary objects. On Venus, where the temperature is significantly higher than on the Earth, fractionation is expected to be less significant. From the isotopic composition one therefore expects mostly information dealing with comparative planetology. Under this aspect, oxygen isotopes (^{16}O , ^{17}O , ^{18}O) will be of particular significance as they permit establishing different fractionation lines for the diverse objects of the Solar system. In the future, analyses of solid samples will require an accurate knowledge of this atmospheric reference.

3. LOSS OF OXYGEN BY CRUST OXIDATION

The second possible fate of oxygen is oxidation of the crust. Assuming FeO represents 5% in mass of the mantle, it may be calculated that a volcanism rate of $\approx 15 \text{ km}^3 \text{ yr}^{-1}$ averaged over 4.5 Gyr is required to provide the chemical reservoir able to absorb the totality of the oxygen contained in an Earth-type ocean. A present rate of only $1 \text{ km}^3/\text{yr}$, or a few km^3/yr , is generally assumed, in order to replenish SO_2 chemically lost to the surface, but no present volcanic activity has still been detected. The knowledge of oxygen fugacity and abundances of key species like CO or SO_2 in the deep atmosphere, and of their vertical profiles, as well as the nature of mineral phases at the surface, would bring unprecedented information relative to the geochemistry of Venus and oxidation processes at the surface.

3.1. Volcanic and tectonic activity

Independent estimates of the present volcanic activity on Venus based on geophysical, geological, and geochemical data generally suggest maximum extrusion rates of approximately $0.4 \text{ km}^3 \text{ yr}^{-1}$. Considering that extrusions are assumed to account for only 5-10% of the total crust production, the upper limit of the crustal growth rate including intrusions may be about $4 \text{ km}^3 \text{ yr}^{-1}$. This value is much smaller than the terrestrial crust production rate of approximately $20\text{-}30 \text{ km}^3 \text{ yr}^{-1}$. On Earth, crust production occurs predominantly at plate boundaries, which provide effective pathways for ascending magma to produce new crust at divergent and convergent margins. On Venus, however, there is no plate tectonics at present. Instead, the convecting mantle is covered by an outer “one-plate” layer, or rather, a stagnant lid, through which magma transport is much more difficult. Such an absence of plate tectonics is reflected on Earth only in the interior of tectonic plates, and in fact, the terrestrial intraplate crust production rate is similar to the assumed maximum crust production rate of Venus. However, no final evidence exists that there is present-day crust production on Venus, at all.

Previous models of the thermal evolution of Venus including mantle differentiation have shown that the high temperatures and the strong convection vigour in the early evolution result in a rapid crustal growth. Associated with the crustal growth is a strong early mantle degassing. Volatiles like H_2O , CO_2 , and noble gases are released into the atmosphere. The evolution of the atmosphere is, therefore, strongly related to the crust production and the associated mantle degassing but also to the capture of in-falling comet-like material enriched in volatile components. In the subsequent evolution, the atmosphere has been fed by continuing crustal growth and mantle degassing. These models assume a continuously evolving planet. On Venus, however, the cratering record of the surface indicates a global or near-global resurfacing event about 750 to 500 Ma ago. The volume that erupted is estimated to exceed the largest igneous provinces on Earth by as much as an order of magnitude. Whether this volcanic activity ceased abruptly or gradually is not clear, yet. Also the explanation of this resurfacing event has been debated diversely. Possible explanations for this catastrophic event include episodic mantle overturning or a transition from a plate tectonic-like convective regime to the present stagnant-lid convective regime. The consequences of the resurfacing for the evolution of the atmosphere and the surface temperature are still uncertain, as well. Models propose an increase of the surface temperature due to a strong release of greenhouse gases. Alternatively, it has been suggested that the

surface temperature did not change significantly due to a chemical-albedo feedback.

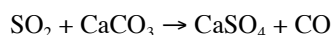
Future models of Venus' mantle convection, thermal evolution, and atmospheric evolution shall provide an explanation for the resurfacing event. For better-constrained models, more precise information on the present state of the atmosphere and the interior structure of the planet including its temperature distribution is needed. To obtain this data base, the knowledge of a possible existence and the amount of present-day crust production is most relevant. Such an objective may be difficult to fully reach from a single descent probe, which would nevertheless give information on atmospheric/ surface composition (and could search for volcanic tracers). Using low altitude balloons, or a network of small entry probes, would bring substantial additional value from this point of view. With the help of the above described interrelations between the various factors influencing the crust production or its rate, more precise present-day values for the mantle temperature, the convection velocity, and the lithosphere thickness can be determined. These parameters can be used, in turn, as boundary conditions for the coupled thermal and atmospheric evolution models in order to lead to a comprehensive understanding of the planet Venus and its evolution.

3.2. Main chemical cycles in the low atmosphere

Several questions concerning the molecular composition of the Venus atmosphere remain unresolved. The most important ones are: (i) Middle atmosphere: "What is O₂ abundance near the cloud tops?" ([30]); (ii) Lower atmosphere: "Better measurements of composition, including vertical and horizontal variation of such species as SO₂, SO, H₂S, Cl₂, COS, and H₂O. In particular, detailed comparison of in-situ and remote observations of H₂O in deep atmosphere" ([31]) ; (iii) Surface-atmosphere interactions: "There is still a pressing need for a deep atmospheric spacecraft to measure the chemical composition of the lower 22 km of the atmosphere. The gases of most interest are H₂O, CO, SO₂, OCS, S₁₋₈, and H₂S, and the method to measure them is probably infrared spectroscopy..." ([32]). To reach a coherent picture of the chemical cycles operating throughout the whole Venus atmosphere, coupled in its lower layers with surface through thermochemical equilibrium processes between vapor and mineralogical phases, requires the simultaneous measurements of the concentration of molecular species, the oxygen fugacity, and, if possible, phenomena signing mixing processes, competing with thermochemical processes in the low atmosphere.

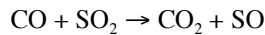
The question of the (never measured) value of the oxygen fugacity near the surface and in the first kilometers above it, is of crucial importance. Given the 17±1 ppm carbon monoxide mixing ratio measured on board Venera 11/12 in the lower Venusian atmosphere (12 km), a 50% confidence interval on such a value extrapolated down to the planetary surface (0 km) would give rise to an order of magnitude incertitude on the calculated oxygen mixing ratio at 735 K, a variation of 10 K yielding a factor 3 error on the inferred value. The most comprehensive study of the redox state of the lower atmosphere of Venus still proposes an almost two orders of magnitude uncertainty of the surface oxygen fugacity, centered at 10-20.85 bars ([32]).

Abundances of gases like SO₂, COS, HCl are controlled by thermochemical reactions with minerals at the surface. The CO₂ pressure is assumed to be maintained through equilibrium with surface calcium silicates. Although thermodynamical calculations are in rather good agreement with observation (temperature, CO₂ pressure), the basic question of the stability of such a system is still unanswered. Concerning SO₂, equilibrium values definitely differ from observed values, and existing measurements significantly differ from each other for unknown reasons. The finding by [33], from UV absorption measurements of SO₂ from the Vega descent probes, that the SO₂ mixing ratio regularly decreases with decreasing altitude from 100 ppm at 40 km altitude, just below the clouds, down to 25 ppm at 10 km altitude, is particularly intriguing. It contradicts the current model of thermochemical equilibrium with calcite :



which results in an equilibrium value of SO₂ mixing ratio at the surface of 100-130 ppmv ([32]), in agreement with the different existing measurements below the clouds, but not with the low value measured by Vega in the low atmosphere. As mentioned by [33], such a vertical variation could be associated with horizontal variations, through the existence of sinks and sources, and therefore of regions where the vertical gradient is reversed. Horizontal coverage, by using balloons, could provide an answer to this question. Equilibrium abundances of main chemical species in the lower scale height of the atmosphere are presented in Figure 5.

Another point mentioned by [33] is the strong link between SO₂ and CO concentrations, through both the gas/surface reaction previously mentioned and the gas/gas reaction :



A simultaneous measurement of CO, O₂ fugacity and SO₂ should allow to better characterize the Venus chemical system. Characterization of surface material, in particular the Fe-bearing minerals, would considerably help in understanding the general equilibrium of low atmosphere. The question of the intensity of the vertical atmospheric mixing by turbulence and large scale dynamical processes deserves to be mentioned. In the absence of any information, it is impossible to derive the vertical SO₂ flux from the vertical gradient observed by [33]. Another important implication is that vertical mixing times t_{mix} are expected to be of the same order as chemical times t_{chem} associated with the main thermochemical equilibria, like the CO/SO₂ equilibrium previously mentioned. If $t_{\text{mix}} < t_{\text{chem}}$, a gas like CO is uniformly mixed with altitude, whereas if $t_{\text{mix}} > t_{\text{chem}}$, thermochemical equilibrium is realized everywhere, and the CO mixing ratio increases with altitude (Fig. 5). Measuring the vertical profiles of reactive species, and temperature, in the 0-10 km altitude range should therefore allow to put constraints on vertical mixing, together with other means, like vertical and horizontal profiles of radioactive tracers (radon).

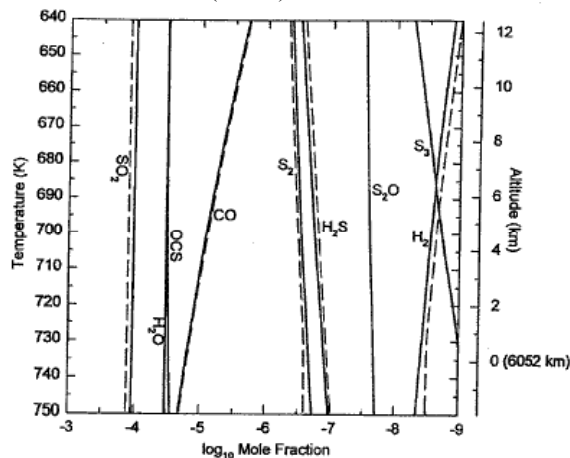


Figure 5: Calculated equilibrium abundances of C, O, N, S, H gases (other than CO₂ and N₂) in the lower atmosphere of Venus (from [32]).

The measurements of :

- the vertical profiles and composition of cloud particles,
 - the vertical profiles of molecular constituents and the oxygen fugacity in the deep Venus atmosphere through in-situ measurements,
 - the radiative fluxes, controlling the greenhouse effect, and the surface mineralogical composition by infrared spectroscopy and imaging,
 - possible tracers of volcanic activity,
- would be of great interest in solving mysteries related to the beginning and evolution of greenhouse

effect, and to its impact on atmospheric chemistry and oxidation of surface minerals.

Together with noble gas (elemental and isotopic composition) and stable isotopes measurements, these observations, which can be made with a great increase in sensitivity and accuracy with respect to observations made from descent probes more than 25 years ago, will allow us to break through in our understanding of Venus and other terrestrial planets formation and evolution.

4. POSSIBLE PAYLOAD OF A VENUS ENTRY PROBE

4.1. Noble gas static mass spectrometer

An isotopic analyzer using a time-of-flight mass spectrometer coupled with a gas separation/purification system might be used. Noble gases are first separated from reactive gases through chemical gettering by using a zirconium getter. In a following step, noble gases are separated from each other by cryotrapping on an activated charcoal bed, cooled by a Stirling machine, yielding three separate fractions : [He, Ne], [Ar], [Kr, Xe], which may be analyzed separately in a static mode (without carrier gas). In this way, it is possible to reach high sensitivity, and to remove a few mass interferences (like ²⁰Ne/⁴⁰Ar), in such a way to measure isotopic ratio with an accuracy better than 1%. This method has been extensively used in the laboratory since fifty years to analyze noble gases in terrestrial and meteoritic samples, and is presently being developed for Mars in-situ exploration [34]. Such a static ToFMS analyzer, could be operated on board the descent probe, by sampling atmosphere around 60 km altitude, and analyzing noble gases during the 1-2 hrs descent of the probe through the atmosphere.

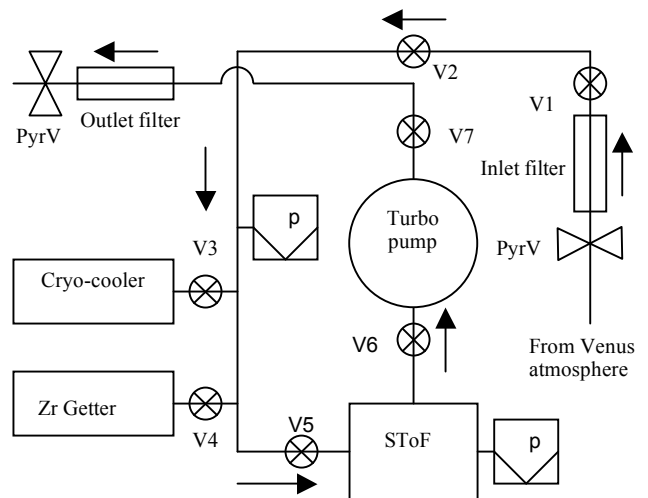


Fig. 6 : Schematic view of the static time-of-flight mass spectrometer and of the separation/ purification line.

4.2. Tunable diode laser spectroscopy (TDLAS) for major constituents and stable isotopes

On Venus, the best altitude range for TDLAS method is the upper atmosphere, including the cloud region (from ≈ 80 km to ≈ 40 km). The accuracy of the measurements at these altitudes will be approximately the same: while descending in the atmosphere, the number of molecules in the cell is increasing, but because of line broadening the absorption remains the same. The best discrimination (isotopic measurements) occurs above 60 km. Below, where the lines broaden, the sensitivity and discrimination degrade progressively. At pressures exceeding 10 bar, the collisional broadening is no more described by Voigt profile, and is poorly parametrized, so the quantities cannot be accurately retrieved from measured absorptions. The TDLAS method is hardly applicable already at 30 km at exterior pressure. It is possible, however, to study this altitude range very important for surface-atmosphere interaction by means of active spectroscopy in a cell, if the gas will be analyzed at reduced pressure. It might be possible to take the advantage of the gas sampling system of a mass-spectrometer, or to employ a dedicated sampling system. The best sensitivity and discrimination is achieved at pressures of 0.1-1 bar.

Table 3 : Characteristics of molecular absorption by species of interest.

Molecule	Spectral range (cm ⁻¹)	Altitude (km)	Abs. Opt. Path : 10 m	Value range	Accuracy
H ₂ O	7295-7315	40-70	0.02-0.1	≈ 30 ppmv	$< 10^{-3}$
		70-90	0.01-0.001	$\approx 10^{-2}$	$\approx 10^{-2}$
		30-40 ⁽¹⁾	≈ 0.15		$\approx 10^{-2}$
HDO ⁽²⁾		≈ 60	TBD	D/H ≈ 150 ⁽³⁾	TBD
¹² C ¹⁶ O ₂	5337-5339	30-TBD	0.001		$< 10^{-3}$
¹³ C ¹⁶ O ₂	5010-5020	TBD	0.05		$< 10^{-3}$
¹² C ¹⁶ O ¹⁸ O	5040-5050	≈ 60 km	0.05		$< 10^{-3}$
¹² C ¹⁶ O ¹⁷ O	5040-5050	≈ 60 km	0.02		≈ 0.01

⁽¹⁾ The lower atmosphere (0-30 km) is as well accessible if a gas sampling system reducing the pressure is possible.

⁽²⁾ Spectroscopic data by [35].

⁽³⁾ In units of SMOW value.

Possible atmospheric targets of TDLAS in Venus atmosphere are numerous, and may be divided in two categories : (i) measurement of CO₂ and/or H₂O isotopic ratios ; (ii) measurements of molecular species (HCl, OCS, HF, H₂S, CH₄, NH₃, HBr, HI). Concerning molecular species, the typical accuracy of the measurements varies from a few ppbv (HF, CH₄) to one ppmv (HCl) and a few tens of ppmv (OCS, H₂S). Concerning isotopes of CO₂ and H₂O, which

are of particular interest, the main characteristics may be summarized as follows.

4.3. A zirconium fuel cell for the measurement of oxygen fugacity

The most comprehensive study of the redox state of the lower atmosphere of Venus still proposes an almost two orders of magnitude uncertainty of the surface oxygen fugacity, centered at $10^{-20.85}$ bars [4]. On the other hand, a direct and continuous measurement of the oxygen mixing ratio from, say, 20 km down to the surface, would provide the lacking key parameter for thermodynamic derivations of a chemically equilibrated Venusian atmosphere, for computing the oxygen budget of the crust-atmosphere system (and, hence, deducing the surface mineralogy) and for modelling the origin and evolution of the planetary atmosphere. Up to now, this parameter remains unknown, constrained by instrument sensitivities (upper limits) and by reasonable thermodynamical and geochemical considerations (lower limits), and leads to conflicting models, describing the atmosphere and lithosphere of Venus as comparatively oxidized or reduced. Moreover, if complementing the already known temperature profile, an oxygen profile would give insight into the chemical homogeneity and possible geochemical layering of the Venusian atmosphere.

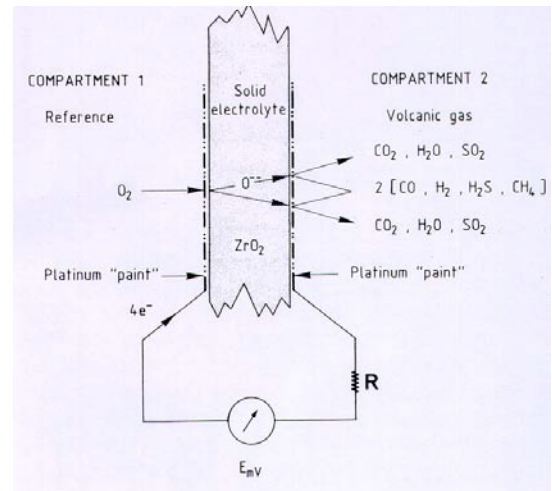


Fig. 7 : Principle of a solid electrolyte oxygen sensor. Basically, it is a fuel cell "burning" the combustible atmospheric gases CO, CH₄, COS, H₂S, S₂ and H₂, into CO₂, SO₂ and H₂O, by means of oxygen ions instead of oxygen molecules. In this case, the quiet combustion is an equilibrium process. The counterpart of the flow of oxygen ions in the electrolyte is an electrical current through the external conductor.

The zirconium solid-electrolyte technology offers the possibility of achieving this goal. With their high

accuracy (*i.e.*, ± 0.01 in $\log P_{O_2}$ units) in the suitable range of P_{O_2} (down to 10^{-30} atm, given the high total pressures involved) and their short response-time, the ZrO_2 oxygen probes with a solid internal reference are well adapted for continuous oxygen measurement during the descent - even very fast - of a Venus lander, or during the flight of an atmospheric vehicle. These probes are very lightweight (*ca.* 2g, including wires), do not need a power supply and deliver an electrical potential ($< 1V$), the radio-transmission of which to the Earth, with a ± 1 mV accuracy, is as straightforward as that of the tension of a thermocouple.

With the presently available technology, a ZrO_2 oxygen sensor (called OES, for Oxygen Electrochemical Sensor, in the following) would start delivering measurements at 12 km altitude (643.2K) down to the surface of the planet (735.3K) and will continue to do so until the radio equipment of the vehicle is destroyed.

4.4. Example of payload

The payload proposed in Table 4 is derived from a proposal to ESA for a descent probe/ balloon flotilla mission to Venus ([36]). Balloons may bring a horizontal sampling capability. Nevertheless, even a single descent probe, without any other platforms (neither balloons floating at low altitude, nor micro-probes released from an orbiter), would be of paramount interest. No orbiter is required in this case, data being transmitted directly to Earth. The payload, which would be partially inherited from the Huygens one, might consist of the following instruments:

- Noble gas analyzer: static ToF MS with a separation/ purification line, consisting of a getter and a cryocooler.
- Gas chromatograph (GC), or GCMS, electrochemical oxygen sensor (OES) and optical gas analyzer (OLGA) (molecular/isotopic composition).
- Infrared spectrometer (atmospheric composition, radiative transfer), Visible/Near Infrared spectro-imager (atmospheric composition, surface mineralogy/morphology on dayside, surface temperature on night side). The VISS (Venus Imaging Solid-state Spectrometer) uses the AOTF technology (Acousto-Optic Tunable System). It may be used for reflectance spectroscopy (0.5-1.2 μm range), in order to determine the mineralogy of surface material, as well as probing of atmospheric gases in the thermal infrared (1.7-4 μm and beyond). Several windows exist, where the transparency length ($\tau=1$) is small (a few hundred meters to a few kilometers). It is divided into a VIS-NIR and a IR instrument. An option could be to use a grating spectrometer (Visible Near-Infrared Spectro-imager VNIR).

- Radioactive tracer detector (APID instrument, for Alpha Particle Ionization Detector).
- Atmospheric sensor package APTIV (p, T sensors, accelerometer).

Table 4 : Main budgets of descent probe payload.

Instrument	Power (average)	Mass (kg)	Volume (Liter)	Data Rate (kbits/s)
MS ⁽¹⁾	5.6	5	1	0.1
GC ⁽²⁾	8	1.5	1.6	0.15*
OES ⁽³⁾	2	0.02	0.01	0.001
OLGA/TDLAS ⁽⁴⁾	1.3	0.4	0.2	1.6*
OLGA/UV ⁽⁵⁾	5	1	1	0.1
VISS/VIS-NIR ⁽⁶⁾	2.5	1	1	5.3*
VISS/IR ⁽⁷⁾	6	1.1	1	0.4*
APID ⁽⁸⁾	0.1-1	2.3	3	0.1
APTIV	0.5	0.7	0.5	0.36*
TOTAL	31.9	13.0	9.31	8.1
Alternative to VISS/VIS-NIR ⁽⁹⁾ :				
VNIS	7	3	4.5	3

⁽¹⁾ Assumed time analysis of 1 hr.

⁽²⁾ data rate : 80 kb per 10 mn analysis.

⁽³⁾ Power : 2 W if heating required ($z > 15$ km), 0 W if not.

⁽⁴⁾ 1 measurement per 5 mn interval assumed..

⁽⁵⁾ 1 measurement per 10 s interval assumed.

⁽⁶⁾ 1 spectro-image per 5 mn interval assumed.

⁽⁷⁾ 1 linear image per minute assumed.

⁽⁸⁾ Option 1 : pulse-type ionization chamber.

⁽⁹⁾ 1 spectro-image per minute assumed.

*Assumed data compression rate : 5

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